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(54) POLYETHERS AND THEIR USE AS BRAKE FLUIDS

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyethers.

It is known from German Patent Application published under No. B 24 109—23.5 to use as hydraulic liquids products which are formed by the reaction of ethylene oxide and/or propylene oxide with di- or tri-ethyleneglycol-monoalkyl ethers or tripropyleneglycol-monoalkyl ethers. These products are prepared by reacting ethyene oxide or propylene oxide alone, or both these substances simultaneously or sequentially (ethylene oxide being the first reactant) with the glycol ethers in the presence of alkaline catalysts.

Liquids prepared by this method, however, no longer meet the requirements for high-quality brake fluids with respect to boiling point, thermal stability, swelling power, viscosity/temperature behaviour and anti-freezing quality. Other properties, such as lubricating power and ageing stability, may be improved by additives.

The inadequacy of these brake fluids is mainly due to the excessively broad molecular weight spectrum obtained under the reaction conditions chosen. When an excess of starting compound is used in the oxalkylation and this excess is recycled after complete reaction, advantageously in a continuous process, the chain length distribution is narrowed and products are obtained which, at a relatively high boiling point, have a low solidification point and thus also a low freezing viscosity.

The excess of starting ether in the oxalkylation reaction, however, is not sufficient to obtain properties required for modern high-efficiency fluids, when ethylene oxide or propylene oxide is reacted alone. Pure oxethylates at the required high boiling point still have a high viscosity and a high solidification point; pure oxypropylates have insufficient thermal stability and show an increased tendency to cause rubber swelling. Mixed oxalkylates also mentioned in the cited specification are generally more suitable than pure oxethylates or oxypropylates, but because of their method of preparation, they do not meet all the requirements.

Surprisingly, it has now been found that, for cooxalkylation to be successful with respect to the obtention of products having the desired low viscosity, not only the presence of propylene oxide is decisive, but simultaneously the position thereof in the ethylene oxide/propylene oxide chain which is added to the starting ether.

The present invention provides a polyether of the formula

$$RO.(CH_2CH_2O)_x(\underset{\substack{|\\CH_3}}{CH_2.CHO})_y(CH_2CH_2O)_z.H$$

in which R is an alkyl radical having from 1 to 4 carbon atoms, x is an integer of from 1 to 3, y is 1 and z is an integer of from 1 to 3.

As is shown in the following Table 1, it can be demonstrated using the tetra- and penta-adducts (i.e. substances having an alkoxy radical and 4 or 5 alkylene oxide units) that the freezing viscosity tends to a minimum in the case where the propylene oxide unit is in a central position in the molecule chain, that is, when at least one, preferably two ethylene oxide units are adjacent to the alkoxy radical, followed by a propylene oxide unit and then one or two ethylene oxide units. In a position immediately adjacent to the alkoxy group, and still more so as the terminal member of the chain, propylene oxide loses its

influence on the viscosity of the product obtained, and the viscosity increases. The decrease of viscosity by determined incorporation of propylene oxide into the molecule is supported by the corresponding alkoxy group, depending on its structure. In the case of ethoxy derivatives, there is no such support because of the identical structure of the ethoxy group and the added ethylene oxide, and the viscosity curve is displaced in this case. The minimum viscosity was attained with a product in which the propylene oxide unit is in the second position behind the alkoxy radical. A long, uninterrupted ethylene oxide chain causes the viscosity to rise to a far higher degree than can be achieved with a corresponding increase of the molecule size by using another alcohol, which fact is proved by comparison of butoxy - tetra - alkyleneglycols with methoxy - penta - alkyleneglycols which, at nearly the same molecular weight, have very different viscosities.

The viscosities at 20°C and at −40°C display in principle an identical behavior, with the exception that in the first case the maximum is achieved by virtue of the group R-propylene oxide — ethylene oxide$_3$, if R does not represent ethoxy-, and in the second case it is achieved by virtue of the group R-ethylene oxide$_3$-propylene oxide. However, the differences between the individual values are less pronounced at 20°C than at −40°C.

Comparative tests of high-degree oxypropylation show that the viscosity at 20°C may still be slightly decreased, but there is no longer any improvement at −40°C, so that the use of an increased amount of propylene oxide is uneconomic.

The polyethers according to the present invention, and mixtures thereof for the manufacture of high-quality brake fluids, can be prepared by the various processes described below, all of which are continuous processes.

In these processes, the starting material is a mono-, di- or triethyleneglycol-monoalkyl ether the alkyl group of which has from 1 to 4 carbon atoms i.e. a compound of the formula

$$RO(CH_2CH_2O)_xH$$

in which R and x have the meanings given above, preferably a diethyleneglycol-monoalkyl ether, or a mixture of any two or more such compounds. This starting material is reacted with ethylene oxide and propylene oxide, preferably in an ethylene oxide: propylene oxide molar ratio of from 1:1 to 1:0.25 at an elevated temperature and pressure and in the presence of an alkaline catalyst.

In a first process according to the invention, an excess of the starting ether is reacted in a first step with propylene oxide and, after removal of excess ether by distillation, the product obtained is reacted in a second step with ethylene oxide. The starting ether is preferably in a trimolar excess, relative to the propylene oxide, in the first step, and the intermediate product is preferably in a tetramolar excess, relative to the ethylene oxide, in the second step.

As mentioned above, the process is carried out continuously, for example in a tube reactor; the excess ether from the first step and preferably the excess intermediate product from the second step, are advantageously recycled to the first and second steps, respectively.

The slight tendency of propylene oxide towards multiple addition because of the secondary hydroxyl group formed during the addition reaction can be countered by using a relatively small excess of starting ether. However, the poor reactivity of propylene oxide requires a correspondingly longer residence time in the reactor.

In the second step, excess propylene oxide adduct obtained in the first step is reacted with ethylene oxide; the excess adduct should be greater than the excess ether in the first step because of the far greater tendency of ethylene oxide towards multiple addition.

Since the oxalkylation process is carried out in two steps, however, the costs involved are higher than for a single-step process.

In a second process according to the invention, ethylene oxide, propylene oxide and an excess of the starting ether relative to the ethylene oxide and propylene oxide, are reacted together and the mixture obtained is distilled under reduced pressure to obtain a sump product consisting of the polyether. The distillate obtained in this process contains the excess starting ether and short-chain reaction products and is advantageously recycled to the process together with that amount of starting ether which has been consumed, and fresh ethylene oxide and propylene oxide.

The heat of reaction liberated by the addition of ethylene oxide units activates addition of the less reactive propylene oxide so that there are obtained products which contain propylene oxide units as the first unit of addition. These intermediate products react at reduced speed and, because of their very low boiling points, form the main constituent of the recycled intermediates, together with a small amount of excess starting ether and short-chain ethylene oxide adducts. These recycled substances, as well as fresh starting ether, are fed back into the process and continue to be oxalkylated. After the process has been worked continuously for a short period, the recycled mixture attains a constant composition which depends on the relative amounts of starting materials used and which governs the structure of the final product. The amount of propylene oxide which is unreacted in the first step suppresses mul-

tiple addition of ethylene oxide, enabling uniform chain growth.

In a modification of the latter process, from one third to two thirds of the ethylene oxide to be reacted is added to the reaction mixture only after complete reaction of the propylene oxide with the starting ether. This can be effected by introducing the appropriate amount of ethylene oxide into the reaction zone at a suitable point, and promotes the primary addition of propylene oxide and the terminal addition of ethylene oxide.

The following Examples illustrate the invention.

Example 1.

In a pressure-resistant tube reactor (internal width 50 mm, capacity 1800 l), 1800 liters per hour of a starting mixture of

1350 l of diethyleneglycol-monomethyl ether = 11 kilomols
225 l of ethylene oxide = 4.6 kilomols
225 l of propylene oxide = 3.5 kilomols

preheated to about 125°C were reacted continuously at a pressure of 33 atm/g in the presence of 2 milliequivalents of KOH/l of mixture as catalyst, and maintained at a temperature of from 200 to 210°C by means of evaporation cooling with the air of pressurized water.

The completely reacted hot mixture was released immediately into a fractionating column having 32 bubble plates and divided at a pressure of 6 mm Hg into a distillate which was recycled into the reactor and a bottom product having a boiling point of about 300°C (ASTM).

After about 12 hours of operation, the recycled distillate had a volume of about 990 l and, from that time on, a constant composition of

15% of diethyleneglycol-monomethyl ether
15% of triethyleneglycol-monomethyl ether
70% of diethyleneglycol - propyleneglycol - monomethyl ether.

This recycled mixture, together with 360 l (3 kilomols) of diethyleneglycol-monomethyl ether (to make up for the discharged product) was subsequently the main component for the continuous co-oxalkylation, besides the two oxides. Its composition was as follows:

38% of diethyleneglycol-monomethyl ether
11% of triethyleneglycol-monoethyl ether
51% of diethyleneglycol - propyleneglycol - monomethyl ether.

The bottom product was used without further work-up as main component of a high-quality hydraulic fluid (see Table 2).

Examples 2 to 5.

In the same reactor and in the same manner, ether mixture, ethylene oxide and propylene oxide were reacted; gradually increased amounts of ethylene oxide (from 80 to 150 l/h) taken from the total quantity of ethylene oxide to be used (225 l) were fed into the second half of the reactor by means of a dosage pump (so-called side current). The results are listed in Table 2, lines c, d, e). At this place of the reactor, the propylene oxide had already reacted to a rate of 90%.

Examples 6 and 7.

While maintaining the side current and using the largest ethylene oxide amount chosen for this purpose (150 l of a total of 225 l/h), and operating in the same manner as indicated in Example 1 (valid also for all following Examples), the molar ratio of ethylene oxide to propylene oxide of 1:0.76 was changed to 1:0.52 (Example 6) and 1:0.33 (Example 7). The total molar number of the alkylene oxides used remained the same, so that the volume was slightly altered (Table 2, lines d, e, f).

The comparison of Example 1 with the following Examples 2 through 7 shows:

1) the decrease of viscosity caused by gradual increase of the ethylene oxide side current (Examples 2 through 5, lines d, 9, 10 of Table 2)
2) the possibility to reduce the propylene oxide amount while maintaining the molar quantity of the total oxide use, without resulting in a rise of the freezing viscosity above the original value.
(Examples 6 and 7, lines d, e, f, 9, 10 of Table 2).

For a comparison, data of mixed oxalkylates obtained by means of hitherto known processes are listed in Table 3, where they are arranged in the same manner as the data of the lower part of Table 2 (lines 1 through 10 of both Tables). All these previous processes tested comparatively are carried out batchwise in pressure vessels without using an excess of one of the reactants. Sometimes, the addition of the oxides is carried out in two steps; the propylene oxide always being added in the second place.

A comparison of the data of Tables 2 and 3 shows that in the process of the invention a high boiling point is attained (lines 8) despite a reduced molar ratio of oxide mixture to oxalkylation component (lines 4) and reduced molecular weight (lines 7) because of the narrow range of chain length. There is also a low freezing viscosity (lines 10) supported by the determined incorporation of the propylene oxide into the adduct chain, despite the relatively small propylene oxide amount in the product.

Key to Tables 2 and 3
M = methanol
MG = ethyleneglycol-monomethyl ether
EG = ethyleneglycol-monoethyl ether
MDG = diethyleneglycol-monomethyl ether
ETG = triethyleneglycol-monoethyl ether
E = ethylene oxide
P = propylene oxide.

TABLE 1

E=ethoxy P=propoxy group

			RPE_3	$REPE_2$	RE_2PE	RE_3P	RE_2P_2 (comparison)	RP_4 (comparison)	RE_4 (comparison)
tetra-adducts	R=methoxy, b.p.=288–293, m.w.=222	c^S 20°	11.95	10.52	10.02	10.95	9.85	9.81	11.3
		c^S −40°	675	585	496	772	619	854	solid
	R=ethoxy, b.p.=297–299, m.w.=236	c^S 20°	11.12	10.94	10.75	11.34			
		c^S −40°	693	641	707	939			
	R=butoxy, b.p.=314–316, m.w.=264	c^S 20°	13.43	12.85	12.42	13.15			
		c^S −40°	778	714	700	989			

			RPE_4	$REPE_3$	RE_2PE_2	RE_3PE	RE_4P
penta-adducts	R=methoxy, b.p.=315–322, m.w.=266	c^S 20°	15.9	15.1	14.8	14.9	15.6
		c^S −40°	1445	1138	1115	1201	1552

TABLE 2

Data of the mixed oxalkylates of Example 1 through 7

Line	Example		1	2	3	4	5	6	7
a	batches (l/h)	Ether, fresh (see line 1)	360	360	360	360	360	350	340
b		ether, circulation	990	990	990	990	990	990	990
c		E in mixture	225	145	125	100	75	115	150
d		E in side current	—	80	100	125	150	150	150
e		E total	225	225	225	225	225	265	300
f		P in mixture	225	225	225	225	225	175	130
g		total amount	1800	1800	1800	1800	1800	1790	1780
1	oxalkylation component fed into the system (see line a)		MDG	MDG	MDG	MDG	MDG	MDG	MDG
2	composition of the oxide mixture	$\frac{P}{E}$ (kg)	1	1	1	1	1	0.66	0.44
3		$\frac{P}{E}$ (kilomols)	0.76	0.76	0.76	0.76	0.76	0.52	0.33
4		$\frac{(E+P)}{\text{oxalk. comp.}}$ (kilomols)	2.7	2.7	2.7	2.7	2.7	2.7	2.7
5	total oxide content	$\frac{(E+P)}{\text{alcohol}}$ (kilomols)	4.7	4.7	4.7	4.7	4.7	4.7	4.7
6	weight % P in final product (rel to total oxide)		30.4	30.4	30.4	30.4	30.4	23.8	18.0
7	data of the final product	mean mol. weight	255	255	255	255	255	252	249
8		boiling point (°C/ASTM)	301	303	301	302	302	301	303
9		viscosity cS 20°	13.1	13.0	12.9	12.8	12.6	12.8	13.3
10		viscosity cS −40°	970	962	932	905	870	890	950

TABLE 3

Data of mixed oxalkylates of different applicants

Line			GAS 1 231 835					GOS 1 593 178
1	Oxalkylation component		M	M	MG	MG	EG	ETG
2	composition of the oxide mixture	$\frac{P}{E}$ (kg)	1	1	1	1.5	1.5	only P used
3		$\frac{P}{E}$ (kilomols)	0.76	0.76	0.76	1.14	1.14	,,
4		$\frac{(E+P)}{\text{oxalk. comp.}}$ (kmols)	3.4	4.4	4.4	4.0	4.0	only P 0.6
5	total oxide content	$\frac{(E+P)}{\text{alcohol}}$ (kmols)	3.4	4.4	5.4	5.0	5.0	3.6
6	weight % P in final product (rel. to total oxide)		39.7	41.7	41.7	49.5	49.5	20.7
7	data of the final products	mean mol. weight	202	252	296	282	296	213
8		boiling point (°C/ASTM)	244	256	272	256	271	262
9		viscosity cS 20°	12.1	16.8	~17	16.5	16.8	10.5
10		cS -40°	930	1569	solid	1563	1663	620

TABLE 3 (Continued)

Line			GOS 2 137 970				
1	Oxalkylation component		MDG	MDG	MDG	MDG	MDG
2	composition of the oxide mixture	$\frac{P}{E}$ (kg)	1.86	1.86	1.5	1.86	1.86
3		$\frac{P}{E}$ (kilomols)	1.41	1.41	1.14	1.41	1.41
4		$\frac{(E+P)}{\text{oxalk. comp.}}$ (kmols)	3.1	3.26	3.15	3.08	3.12
5	total oxide content	$\frac{(E+P)}{\text{alcohol}}$ (kmols)	5.1	5.26	5.15	5.08	5.12
6	weight % P in final product (rel. to total oxide)		40.8	43.4	38.9	42.2	42.3
7	data of the final products	mean mol. weight	276	287	282	281	283
8		boiling point (°C/ASTM)	300	305	300	297	298
9		viscosity cS 20°	not stated				
10		cS −40°	1640				

WHAT WE CLAIM IS:—

1. A polyether of the formula

$$RO.(CH_2CH_2O)_x(\underset{\underset{CH_3}{|}}{CH_2.CHO})_y(CH_2CH_2O)_z.H$$

in which R is an alkyl radical having from 1 to 4 carbon atoms, x is an integer of from 1 to 3, y is 1 and z is an integer of from 1 to 3.

2. A process for the continuous preparation of a polyether according to claim 1 by reacting an ether of the formula

$$RO(CH_2CH_2O)_xH$$

in which R and x have the meanings specified in claim 1, or a mixture of any two or more such compounds, with ethylene oxide and propylene oxide at an elevated temperature and pressure in the presence of an alkaline catalyst, which comprises reacting an excess of the ether(s) in a first step with propylene oxide and, after removing the excess ether(s) by distillation, reacting an excess of the product(s) obtained in a second step with ethylene oxide.

3. A process according to claim 2, wherein, in the first step, the ether(s) is(are) in a trimolar excess relative to the propylene oxide.

4. A process according to claim 2 or claim 3, wherein, in the second step, the product(s) obtained is(are) in a tetramolar excess relative to the ethylene oxide.

5. A process according to any one of claims 2 to 4, wherein the excess ether(s) removed prior to the second step is(are) recycled to the first step.

6. A process for the continuous preparation of a polyether according to claim 1 by reacting an ether of the formula

$$RO(CH_2CH_2O)_xH$$

in which R and x have the meanings specified in claim 1, or a mixture of any two or more such compounds, with ethylene oxide and propylene oxide at an elevated temperature and pressure in the presence of an alkaline catalyst, which comprises reacting together ethylene oxide, propylene oxide and an excess of the ether(s) relative to the ethylene oxide and propylene oxide and distilling the mixture obtained under reduced pressure to obtain a sump product consisting of the polyether.

7. A process according to claim 6, wherein the distillate is recycled to the reaction.

8. A modification of the process according to claim 6 or claim 7, wherein from one third to two thirds of the ethylene oxide is added to the reaction mixture only after complete reaction of the propylene oxide and the ether(s).

9. A process according to any one of claims 2 to 8, wherein the ether is a diethyleneglycolmonoalkyl ether or a mixture of any two or more such compounds.

10. A process according to any one of claims 2 to 9, wherein the molar ratio of ethylene oxide to propylene oxide is from 1:1 to 1:0.25.

11. A process for the preparation of a polyether according to claim 1, carried out substantially as described in any one of Examples 1 to 7 herein.

12. A polyether according to claim 1 whenever prepared by a process according to any one of claims 2 to 11.

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